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Experimental Study of Monazite-Water Interaction from 21 to 300ºC

Franck Poitrasson, **Eric H. Oelkers**, **Jacques Schott** & **Jean-Marc Montel**

Laboratoire de Géochimie, CNRS-Université Paul Sabatier, 38, rue des 36 Ponts, 31400, Toulouse, France

Introduction

Monazite (La,Ce,Nd,Th)PO_4 is a major host mineral for lanthanides and thorium in the continental crust. Hence, studies of continental waters or fluid-rock interaction using these elements should take account the behaviour of this mineral in aqueous solutions. Furthermore, monazite is a key mineral for U-Th-Pb geochronology; ceramics with the monazite structure and composition are actively studied as potential nuclear waste forms.

Methods

Monazite dissolution studies have been performed in aqueous solutions at temperatures ranging from 21 to 300ºC and pH from 2 to 9. The minerals studied included a natural homogeneous monazite as well as synthetic $LaPO_4$, $NdPO_4$ and $GdPO_4$ with granulometries ranging from 5 to 50 microns. X-ray diffraction spectra verified the structure of the synthetic minerals. These dissolution studies consisted of batch experiments lasting from 10 to 33 months, with regular sampling intervals. The initial solution/mineral ratio was of 200 by weight and the ionic strength of the solution was fixed to 0.01 Molar, adjusted with NaCl if necessary. For each fluid sample, the pH was determined by potentiometry and element concentrations were measured using an ICP-MS fitted with a desolvation unit to analyse phosphorous at the sub-ppb level. Solubility products were determined after speciation calculations involving the EQ3 code (Wolery, 1992) using an updated database.

Results

The time needed to reach stable concentration of dissolved elements in reacting solutions varied greatly, depending on the monazite sample and temperature. For the experiments with synthetic monazite at temperatures below 100ºC, equilibrium was reached in less than two months. At higher temperatures, the concentrations were not stable after 10 months, but this did not affect the calculated solubility products. For the experiments involving natural monazite, stable elemental concentrations were not attained after 33 months, particularly for the experiments of high pH and temperatures.

This suggests that ongoing reactions occurred between monazite and the fluid, as shown by the incongruent dissolution observed in most experiments with natural monazite. For instance, the Th/Nd ratio measured in the solution appears to decrease below stoichiometric values as the temperature increases, and this effect is especially marked at mildly acidic pH. Preliminary scanning electron microscopy observations, aided with energy dispersive chemical characterisation and X-ray photoelectron spectroscopy revealed that under these conditions, Th reprecipitate on the monazite surface, probably as a phosphate or a hydroxide. This experimental result is consistent with those from studies of monazite-fluid interactions occurring in nature showing that during monazite alteration and dissolution, Th is often reincorporated in the mineral, be it in the form of a newly precipitated phase or through reincorporation in the crystalline lattice (Poitrasson et al., 1996; Poitrasson et al., 2000). For the synthetic minerals, the REE/P elemental ratios measured in solution were also very far from stoichiometry. This is interpreted in terms of preferential release of elements introduced in excess during mineral synthesis and should therefore not affect the validity of the calculated solubility products.

The pKs determined at 21ºC for $LaPO_4$, $NdPO_4$ and $GdPO_4$ decreased from 27.8 to 25.8, suggesting an atomic number trend. The data on synthetic $NdPO_4$ also exhibit a retrograde solubility for the temperature range 21-300ºC (Figure 1). This trend agrees well with previous thermodynamic calculations for this temperature range (Marinova & Yaglov, 1976; Wood & Williams-Jones, 1994).

Furthermore, the solubility products determined for synthetic $NdPO_4$ differ by less than one order of magnitude with partial solubility product estimates based on the natural monazite dissolution experiments (Figure 1). This suggests that the incongruent dissolution observed with the natural monazite occurs close to equilibrium and the solubility product of this phase can be approximated with an ideal solid-solution model. Finally, the pKs determined on the basis of these monazite dissolution experiments are similar to slightly higher compared to results obtained on hydrous rare earth phosphates (see Liu & Byrne, 1997, and references therein). This may be taken as an indication of the good consistency among the various sets of solubility products data. Nevertheless, a detailed study of the monazite surface after the experiments should confirm if the values reported in this study reflect true monazite solubility products or the properties of a hydrous layer formed during the mineral-water experiments.

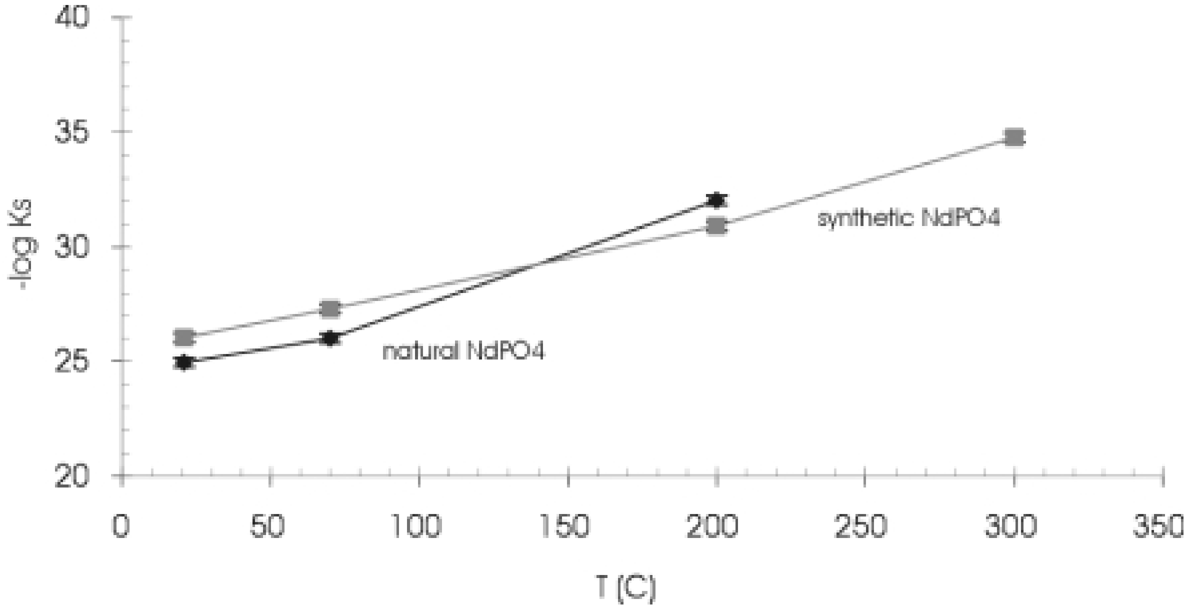

Figure 1: Solubility product of synthetic $NdPO_4$ and partial solubility product of natural monazite

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